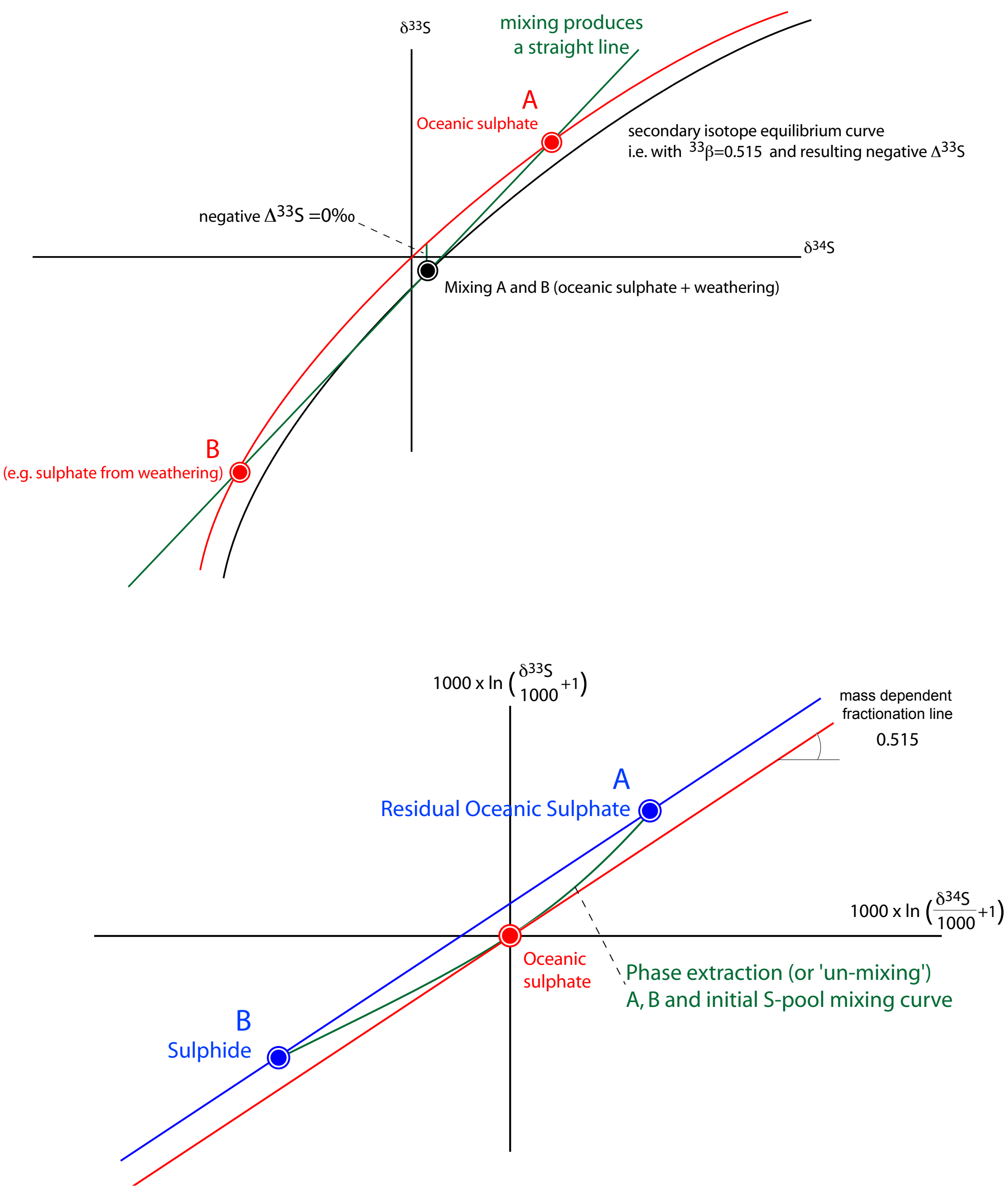
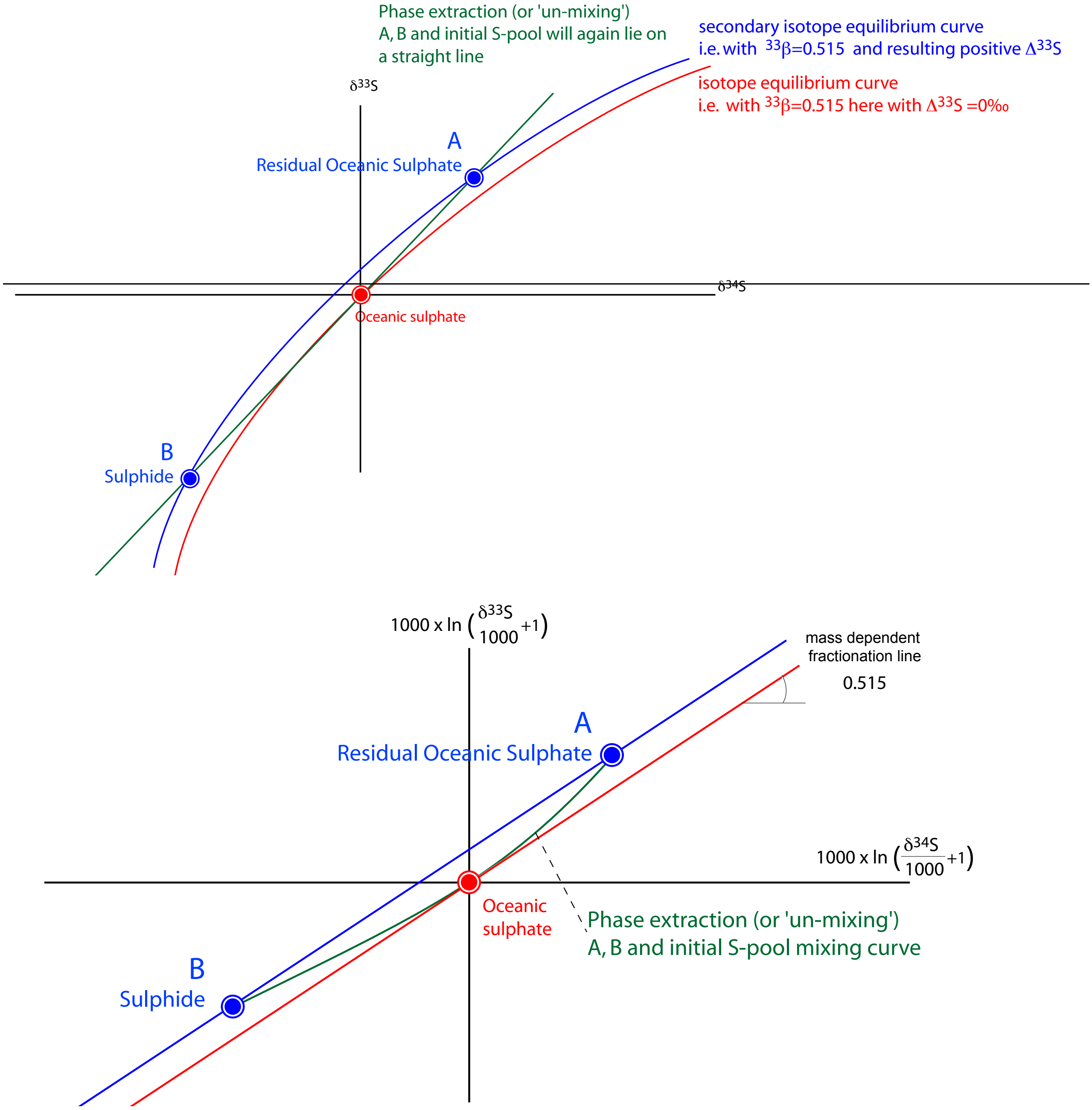
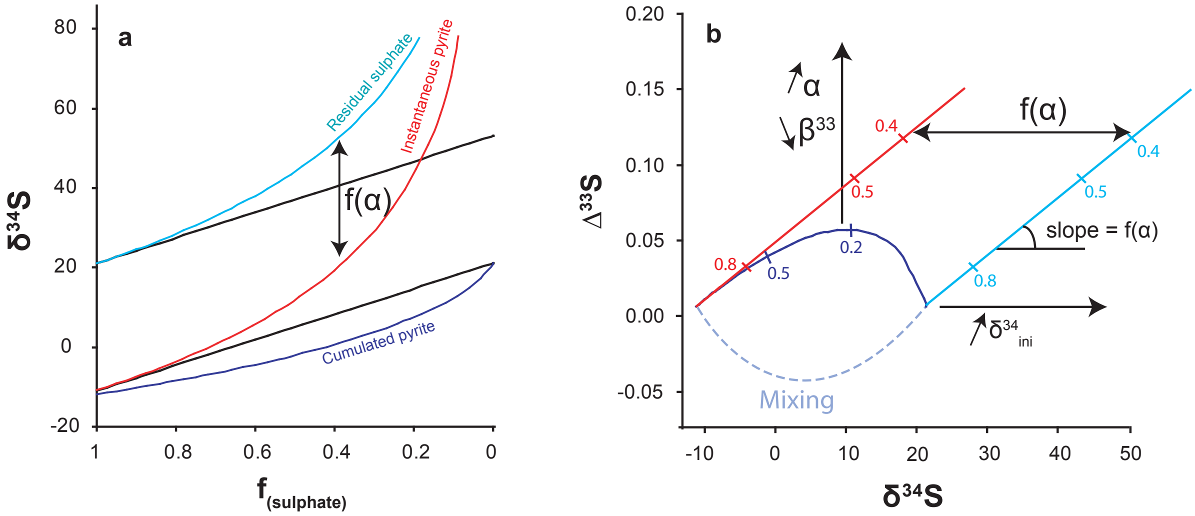


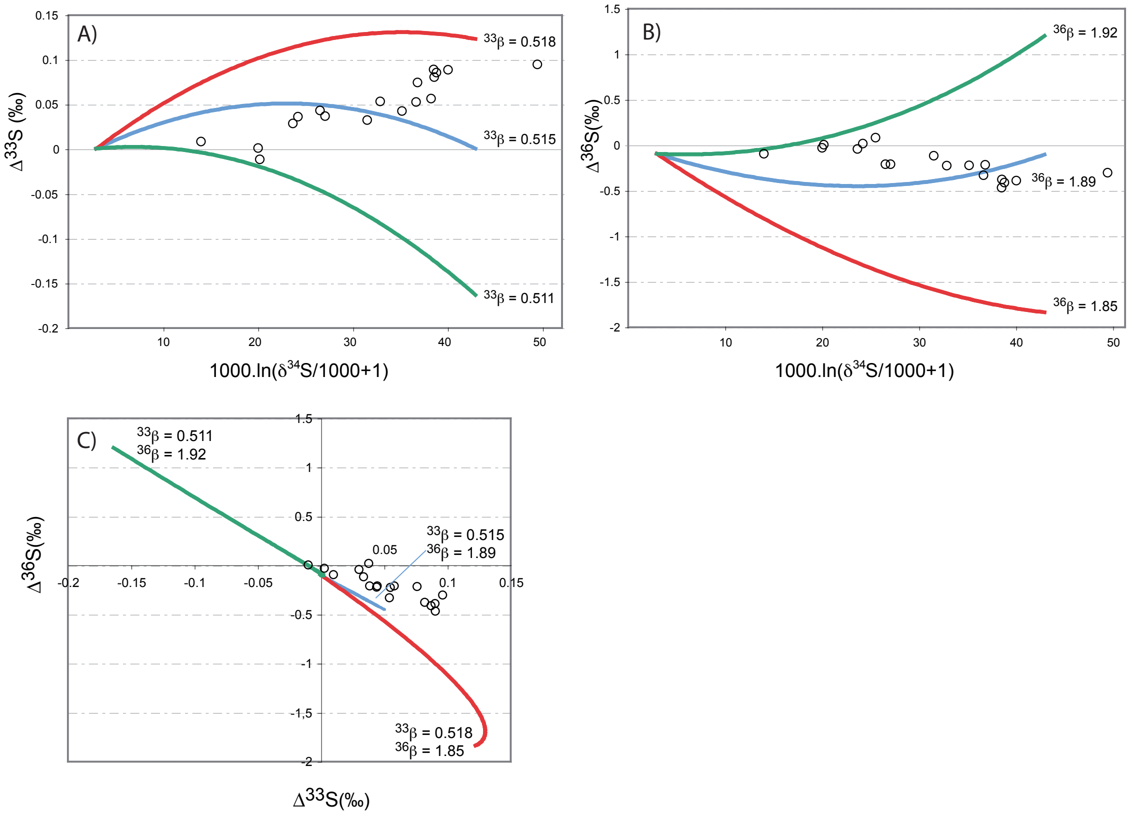
Supplementary Figure 1: Two representations of the relationship between $\delta^{33}S$, $\delta^{34}S$ and non-zero $\Delta^{33}S$-values resulting for a mixing of two pools with different sulphur isotopic composition, yet with $\Delta^{33}S$ = 0‰. Green line is derived from equation [9]. Figure not to scale.



Supplementary Figure 2: Two representations of the relationship between $\delta^{33}S$, $\delta^{34}S$ and non-zero $\Delta^{33}S$-values resulting for phase extraction (or un-mixing) of two pools A and B at isotope equilibrium from a reservoir with $\Delta^{33}S$ = 0‰. Mass conservation effects lead both A and B to have slightly positive $\Delta^{33}S$. Green line is derived from equation [9]. Figure not to scale.



Supplementary Figure 3: Schematic isotopic evolution of the residual sulphate reservoir, instantaneous and cumulative pyrite during a Rayleigh (i.e. open-system) distillation process. **a)** $\delta^{34}S$ vs $f_{(sulphate)}$ calculated from equation [10]. **b)** $\Delta^{33}S$ vs $\delta^{34}S$ calculated from equations [8 and 10] for a $^{34}\alpha_{pyr\text{-}sulph}$ of 0.970 and an initial $\delta^{34}S$ of 21 ‰. All calculations assume $^{33}\beta$-values corresponding to equilibrium (i.e. 0.515).



Supplementary Figure 4: A), B) and C) $\delta'^{34}S$ and $\Delta^{33}S$ and $\Delta^{36}S$ relationships predicted for sulphur isotope compositions of oceanic sulphate in a steady state assumption determined for a series of $^{33}\beta$-values. Open circles are data obtained in this study and given in the Supplementary Table 1.

Supplementary Table 1: **Sample** is the name of the sample. CRS are samples from Carmelo quarry. TeS from Terconi quarry and CA and CAS from Camil quarry. **δ^{34}S. Δ^{33}S and Δ^{36}S** are expressed in ‰ vs CTD. **FeS_2** is the content of pyrite in %. **CAS** is the content of Carbonate Associated Sulphate in ppm. Nd indicates that the CAS content was not determined. Johnston et al. 2005 indicates these data have been compiled from Johnston et al. 2005. Errors are given in the method section.

Sample	$\delta^{34}S_{pyr}$	Δ^{33}_{pyr}	Δ^{36}_{pyr}	FeS_2
CRS 0	-8,97	0,10	-0,10	0,01
CRS 3	-9,87	-0,02	-0,20	0,07
CRS 5	-5,04	-0,06	0,17	0,09
CRS 11	-3,84	0,04	-0,34	0,03
CRS 13	-3,22	0,03	-0,73	0,75
CRS 16	-5,37	0,07	-0,58	3,06
CRS 19	12,21	0,09	-0,77	0,15
CRS 21	26,21	0,06	-0,37	0,05
CRS 23	1,65	0,06	-0,74	0,54
CRS 30	-3,93	0,16	-1,39	3,01
CRS 31	0,32	0,11	-0,88	0,84
CRS 32	8,94	0,08	-0,83	0,43
CRS 35	16,97	0,07	-0,58	0,18
CA -0.63	8,88	0,06	-0,72	0,30
CA -6.65	3,74	0,08	-0,71	1,03
CA -20.6	4,36	0,04	-0,49	0,44
CAS -34	0,39	0,05	-0,55	0,53
CAS -40	2,91	0,03	-0,36	0,53
CAS -60	8,28	0,04	-0,50	0,32
CAS -80	7,07	-0,01	-0,30	0,25
CAS- 96	6,13	0,02	-0,40	0,12
CAS -106	11,61	0,06	-0,51	0,64
CAS -114	7,65	0,06	-0,50	0,17
TeS 22	17,23	0,00	-0,13	0,33
TeS 24	25,67	0,04	-0,31	0,76
TeS 26	24,73	0,02	-0,17	0,40
TeS 28	24,78	0,06	-0,39	0,60
TeS 30	25,38	0,01	-0,08	0,81
TeS 32	15,83	0,04	-0,52	0,69
TeS 34	21,71	0,04	-0,32	0,64
TeS 36	13,57	0,05	-0,60	0,71
TeS 38	17,90	0,01	-0,28	0,60
TeS 46	28,85	-0,03	0,32	0,23
TeS 48	18,66	-0,01	-0,15	0,18
TeS 50	25,90	-0,02	0,19	0,13

Sample	$\delta^{34}S_{CAS}$	Δ^{33}_{CAS}	Δ^{36}_{CAS}	CAS
CRS 1	23,88	0,03	-0,03	98
CRS 2	16,52	0,03	-0,43	Barite
CRS 8	33,35	0,03	-0,43	13
CRS 13	31,95	0,03	-0,11	40
CRS 16	27,37	0,04	-0,20	74
CRS 19	44,00	Nd	0,09	69
CRS 21	50,64	0,10	-0,30	25
CRS 23	37,44	0,08	-0,21	16
CRS 25	35,74	0,04	-0,22	24
CRS 28	38,94	0,06	-0,20	34
CRS 32	39,20	0,09	-0,46	68
CRS 35	37,27	0,05	-0,32	23
CAS -60	39,49	0,09	-0,40	106
TeS 9	14,02	0,01	-0,09	Nd
TeS 32	20,15	0,00	-0,02	69
TeS 40	20,33	-0,01	0,01	25
Johnston et al 2005[ref.1]	17,03	-0,02	-0,02	Nd
Johnston et al 2005[ref.1]	16,42	-0,01	-0,10	Nd
Johnston et al 2005[ref.1]	17,42	-0,01	-0,02	Nd
Johnston et al 2005[ref.1]	20,97	-0,01	-0,18	Nd
Johnston et al 2005[ref.1]	23,10	0,00	-0,16	Nd
Johnston et al 2005[ref.1]	19,94	0,01	-0,12	Nd
Johnston et al 2005[ref.1]	21,39	0,01	-0,05	Nd
Johnston et al 2005[ref.1]	19,15	0,02	-0,17	Nd

Supplementary Reference:

1. Johnston, D. T., Wing, B. A., Farquhar, J., Kaufman, A. J., Strauss, H., Lyons, T. W. & Canfield, D. E. Active microbial sulfur disproportionation in the Mesoproterozoic. *Science* **310**, 1477-1479 (2005).